Title: Development of Comprehensive Detailed and Reduced Reaction Mechanisms for Synagas and Hydrogen Combustion

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ABSTRACT

Objective

This project aims to develop the tools necessary for the design of future coal derived synthesis-gas (syngas) and hydrogen (SGH) fueled combustion turbines. A set of benchmark experiments and computations will be carried out to map: the flame speeds, auto-ignition characteristics, and extinction limits of SGH-oxidizer mixtures over a wide range of mixture compositions, inlet temperatures and pressures. These global values will in turn be used to develop comprehensive detailed and reduced kinetic models for $H_2/CO/H_2O/O_2/N_2$ chemistry. The spatially-resolved flame structure and species time-histories will also be studied in detail to facilitate mechanism optimization. Additionally, the proposed experimental database will be of practical use in determining the desired syngas compositions for optimal IGCC operation, as well as improving the design and operation of internal combustion engines fueled by hydrogen.

Accomplishments to Date

An experimental and numerical study, using uncertainty analysis of the most important parameters, is conducted to evaluate the mechanism for the combustion of $CO+H_2$ mixtures at high pressures in the range 15–50 bar and temperatures from 950 to 1100 K. Experiments are performed in a rapid compression machine. Auto-ignition delays are measured for stoichiometric compositions of $CO+H_2$ containing between 0 and 80% CO in the total fuel mixture. The experimental results show an unequivocal monotonic increase as the proportion of CO in the mixture is raised. Comparisons are made also with the measured ignition delays in mixtures of H_2 with increasing dilution by N_2, corresponding to the proportions of CO present. These times also increase monotonically, albeit with a greater sensitivity to the extent of dilution than those measured in the $CO+H_2$ mixtures. By contrast, numerical simulations for the same mixtures, based on eight existing kinetic models for $CO+H_2$ combustion display a qualitative discrepancy as there is virtually no sensitivity of the ignition delay to the changing ratio of $CO+H_2$, certainly up to 80% replacement. Global uncertainty analyses are then applied to the kinetic model in order to trace the origins of this discrepancy. The analyses take into account the uncertainties in all rate parameters in the model, which is a pre-requisite for evaluation against ignition delay data. It is shown that the reaction rate constant recommended by Baulch *et al*. for the HO_2+CO reaction, at temperature around 1000 K, may be up to a factor of 10 too high and that lowering this rate corrected the qualitative anomaly between experiment and numerical prediction.

In addition to the above RCM study, we examine the high pressure oxidation of dilute CO mixtures doped with 150–200 ppm of H_2 behind reflected shock waves up to 600 atm. The experimental data are collected in the UIC high pressure single pulse shock tube. Simulations using a previously published reaction model show that within experimental error the kinetic model is able to capture the experimental trends for the lower pressure data sets (average nominal pressures of 24 and 43 bars). However, the model under predicts the CO and O_2 decay and subsequent CO_2 formation for the higher pressure data sets (average nominal pressures of 256 and 450 bars). With updated rate parameters for $HO_2+OH=O_2+H_2O$ the model is found to reconcile the elevated pressure data sets.

Future Work

Ignition and oxidation chemistry at high pressures will be studied in a rapid compression machine. This configuration will provide the pressure history and auto-ignition time of homogeneous SGH mixtures over a wide range of fuel/oxidizer compositions and initial conditions. In addition, the counterflow twin-flame apparatus will be employed for the measurements of laminar flame speed and strain-induced extinction limits of premixed SGH flames. In the proposed experiment, water is first atomized by heated nitrogen, and then injected into a heated vaporizer. Subsequently, the water vapor+N_2 mixture is combined with other gases (e.g. O_2, additional N_2, H_2, and CO) to form a combustible mixture of the desired composition. All flow circuits are electrically heated and insulated. The two dimensional flow-field will be measured using Digital Particle Imaging Velocimetry. This experimental configuration will also allow subsequent, detailed mapping of the flame structure using laser-based optical diagnostics.

Experimental conditions will be simulated using detailed chemistry currently available in the literature. Comparison of experimental and computational results will enable the re-evaluation and optimization of current mechanisms. In addition, several key reactions will be studied by ab initio quantum chemistry calculation and master equation modeling, a collaborative study among the PI and co-PIs of this grant. These reactions include, for example, $CO+HO_2\rightarrow CO_2+OH$, $HO_2+HO_2\rightarrow H_2O_2+O_2$, and $OH+HO_2\rightarrow H_2O+O_2$, all of which have a notable influence on SGH oxidation rates under high-pressure, low-to-intermediate temperature conditions. All of the reactions in question have complex temperature and pressure dependences that cannot be easily resolved through mechanism optimization.

List of Publications/Presentations

1. G. Mittal, C.J. Sung, M. Fairweather, A.S. Tomlin, J.F. Griffiths, and K.J. Hughes, "Significance of the HO_2+CO Reaction during the Combustion of CO+H_2 Mixtures at High Pressures," Proceedings of the Combustion Institute, Vol. 31, submitted.
2. R. Sivaramakrishnan, A. Comandini, R.S. Tranter, K. Brezinsky, S.G. Davis, and H. Wang, "Combustion of CO/H_2 mixture at elevated pressures," Proceedings of the Combustion Institute, Vol. 31, submitted.
3. X. You, E. Goos, C.J. Sung, and H. Wang, "Reaction Kinetics of $CO+HO_2\rightarrow$products: ab initio Study and Master Equation Modelling," Poster Section of the 31st International Symposium on Combustion, submitted.

Students Supported under this Grant

1. Kamal Kumar, graduate student in the Department of Mechanical and Aerospace Engineering, Case Western Reserve University.
2. Xiaoqing You, graduate student in the Department of Aerospace and Mechanical Engineering, University of Southern California.